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Gas-Phase Reactions of X_3M-NCR and X_3M-CNR Donor-Acceptor Complexes (M=Al,GA;X=H,Cl,CH_3;R=H,CH_3)

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Gas-phase reactions of X_3M-NCR and X_3M-CNR donor-acceptor complexes (M=Al,Ga; X=H,Cl,CH_3; R=H,CH_3).

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Carbon contamination is one of the major problems during the CVD of group 13 binary nitrides MN from organometallic precursors. Recently we proposed that carbon incorporation in MN is attributed to the metal-carbon bonding in the gas-phase with formation of organometallic heterocycles. To further explore processes of metal-carbon and metal-nitrogen bond formation, model complexes X_3M-NCR and X_3M-CNR (M=Al,Ga; X=H,Cl,CH_3; R=H,CH_3), metal cyanides X_2MCN and X_2MNC and their oligomers $[X_2MCN]_n$ (n=2,3,4) have been chosen for the present investigation. Geometries, relative energies, vibrational frequencies, and thermodynamic parameters of dissociation and elimination reactions are predicted at B3LYP level of theory with full-electron pVDZ basis set. All structures were fully optimized with subsequent vibrational analysis. Gaussian 94 set of programs was used throughout.

Results of this study indicate competitiveness of gallium-carbon and gallium-nitrogen bond formation. Predicted dissociation enthalpies of metal-carbon bonded complexes are about 15 kJ mol^{-1} *higher* compared to dissociation enthalpies of metal-nitrogen bonded isomers both for Al and Ga. For X_2MCN species, Ga-C and Al-N bonding is found to be preferable compared to Ga-N and Al-C, in qualitative agreement with Pearson's HSAB concept. Relative stability of X_2MCN forms is increasing with increasing of electronegativity of terminal group X both for Al and Ga: CH_3<H<CN<Cl. RX elimination reactions with dimerization of X_2MCN are extremely favorable in case of X=H,CH_3; in contrast, for X=Cl dissociation processes are predominant.